Gas Storage

Structural Transition and Tuning of tert-Butylamine Hydrate**

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Gas hydrates, or more generally clathrate hydrates, are a type of inclusion compound and take the form of nonstoichiometric solid crystalline materials formed from water and small guest molecules.[1] Under sufficient pressure of the guest material and at specific temperatures, 3D hydrate structures are formed by the stacking of polyhedral cages of hydrogen-bonded water molecules. Suitably sized guest molecules are enclathrated in cages and their presence stabilizes the compounds formed. Although the guest molecules are physically enclosed within the cages, there are no direct chemical bonds between host water molecules and guest molecules.

In general gas hydrates form three distinct structural families known as structure I (sI), structure II (sII), and structure H (sH), which differ in the combination of cage types required to build a 3D structure.[2] In addition, there are a variety of more complex clathrate hydrate structures, labeled as types III–VII[2] and structure T (sT).[3] It is clear that many of the physical attributes of gas hydrates remain unknown and thus need to be examined in more detail. The gas hydrates are of particular interest in the fields of energy research and environmental science because of the possible applications for the storage of natural gas,[4] sequestration of CO_2 in the deep ocean,[5] and separation of greenhouse gases from flue gas.[6] It is noteworthy that for lowering the pressure of hydrate formation without significant reduction of the capacity to store CH_4, the use of sH hydrate was suggested.[7] Many experimental and theoretical works to understand

macroscopic phase behavior and microscopic structural characteristics of the pure and mixed hydrates have been reported.[8–12] Most recently, we proposed a tuning mechanism to increase the storage capacity of hydrogen in double hydrogen hydrate.[13]

Herein, we report a structural transition of the simple amine hydrate to produce a novel double (CH_4 + tBuNH$_2$) hydrate as confirmed by using microscopic analytical methods. Powder X-ray diffraction (PXRD) was adopted as the primary method to identify the structure of the gas hydrates and to provide lattice parameters. More importantly, the distribution of guest molecules over the hydrate cages was investigated by NMR spectroscopy, as it is imperative to establish a mutual consistency between the structures from PXRD and the structure-specific chemical-shift signatures from NMR spectroscopy to obtain a more complete description of the hydrates. In addition, the corresponding hydrate compositions were determined from a quantitative analysis of the NMR spectroscopic results. We note that during sample preparation in a high-pressure vessel, the composition of the aqueous phase continuously changes. However, for this work we have focused only on the final equilibrium compositions that are spontaneously determined by the pressure of CH_4 gas, system temperature, and initial concentration of tBuNH$_2$.

The tBuNH$_2$ clathrate hydrate, $16(CH_3)_3CNH_2 \cdot 156 H_2O$, which Jeffrey designated as a type VI structure,[2] is a true clathrate as there is no evidence of hydrogen bonding between host water and guest amine molecules. tBuNH$_2$ molecules occupy large complex cages with 17 sides $(4^3 5^9 6^2 7^3)$ while the small cages $(4^4 5^4)$ remain empty.[14] Figure 1 represents the PXRD patterns of both pure tBuNH$_2$ and double (CH_4 + tBuNH$_2$) hydrate at 113.15 K. According to a previous report,[14] the structure of pure tBuNH$_2$ hydrate is cubic (space group $I\bar{4}3d$) with a unit cell dimension of 18.81 ± 0.02 Å. The PXRD patterns of pure tBuNH$_2$ hydrate samples are consistent with the reported single-crystal structure;[14] the slightly smaller unit cell dimension of 18.7117 ± 0.0019 Å arises from the different temperatures at which the parameter was measured. In Figure 1a, all of the observed reflections for pure tBuNH$_2$ hydrate were attributed to type VI structure,[2] as indexed by the Checkcell program.[15] However, it should be noted that there are clear structural differences when we compare the PXRD patterns for pure tBuNH$_2$ hydrate with those of the double (CH_4 + tBuNH$_2$) hydrate. The introduction of CH_4 molecules as guests changes the structure of the pure tBuNH$_2$ hydrate. Preliminary X-ray results suggested that the transformed structure is a cubic sII hydrate, $16S \cdot 8L \cdot 136 H_2O$, with space group $Fd3m$. Because the ideal mole ratio of liquid guest (tBuNH$_2$) is 5.6 when it completely fills the large cages of the host (water), we chose to prepare a double (CH_4 + 5.6 mol% tBuNH$_2$) hydrate to verify the structural transition. The collected PXRD patterns were indexed by using the Checkcell program,[15] and the unit cell dimension was determined to be 17.3060 ± 0.0033 Å (see Supporting Information). The resulting refined pattern (Figure 1b) agrees with the reported value for a face-centered-cubic sII hydrate with $a = 17.31 \pm 0.01$ Å.[16]

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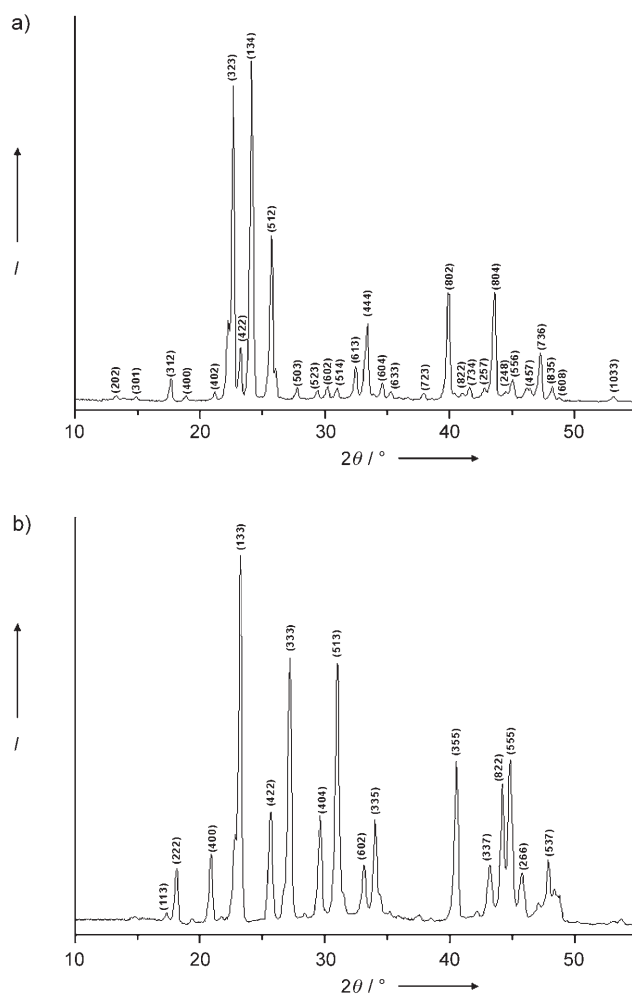
a)

b)

Figure 1. Powder X-ray diffraction patterns: a) pure tBuNH$_2$ hydrate, $a = 18.7117 \pm 0.0019$ Å; b) double (CH$_4$ + tBuNH$_2$) hydrate, $a = 17.3060 \pm 0.0033$ Å.

One of the objectives of this work was to determine the guest distribution of the two types of guest molecules and to use this information to find the equilibrium composition of the double hydrate. Although the 5^{12} cages are common to many hydrate structures, the symmetry and size of these small cages in the structures are somewhat different and their interactions with guest molecules are also different.[17] Accordingly, encaged guest molecules show different chemical shifts in the NMR spectrum which were used for structural assignments and the identification of guest distribution in cages of pure tBuNH$_2$ hydrate and double (CH$_4$ + tBuNH$_2$) hydrate that range from a concentration of tBuNH$_2$ from 9.3 to 1.0 mol%. Figure 2 shows ^{13}C magic-angle spinning (MAS) NMR spectra of pure tBuNH$_2$ hydrate and double (CH$_4$ + tBuNH$_2$) hydrate, which were used to assign the chemical shifts of tBuNH$_2$ molecules as well as those of CH$_4$ molecules in the hydrate cages. The spectrum of pure tBuNH$_2$ hydrate (Figure 2a) is consistent with the tBuNH$_2$ molecules occupying the large cages of this hydrate, as attested by signals at $\delta = 47.3$ (-C(CH$_3$)$_3$) and 31.6 ppm (-C(CH$_3$)$_3$); the signal intensities reflect the molecular formula. Figures 2b and c show the ^{13}C NMR spectra of

double (CH$_4$ + tBuNH$_2$) hydrate (tBuNH$_2$ concentrations of 9.3 and 7.0 mol%, respectively), which both have CH$_4$ and tBuNH$_2$ as guest molecules. The CH$_4$ molecules occupy only the small cages of the double hydrate, as indicated by a single signal at about $\delta = -4.7$ ppm. At the same time, tBuNH$_2$ molecules are present in the large cages, which can be identified by two resonances ($\delta = 46.5$ and 33.1 ppm). However, at these concentrations of tBuNH$_2$, the pure tBuNH$_2$ hydrate and the double (CH$_4$ + tBuNH$_2$) hydrate are found to coexist as the NMR signals characteristic of both hydrates appear downfield of the NMR spectrum. As the concentration of tBuNH$_2$ decreases further, the relative amount of double hydrate increases so that the number of encaged CH$_4$ molecules in the small cages also increases. When the concentrations of tBuNH$_2$ were 5.6 or 4.5 mol% (Figures 2d and e), only the double hydrate was found, as just three peaks were obtained for the double (CH$_4$ + tBuNH$_2$) hydrate. In contrast, pure sI CH$_4$ hydrate also formed in addition to the double hydrate (sII) when the concentration of tBuNH$_2$ was lowered to 3.0 mol% and 1.0 mol% (Figures 2 f and g).

The distribution of CH$_4$ molecules throughout the cages in the pure CH$_4$ hydrate and in the double hydrate was investigated for concentrations of tBuNH$_2$ from 3.0 to 1.0 mol%; expanded NMR spectra are presented in Figure 3. In the ^{13}C NMR spectra of the sII double hydrate, two CH$_4$ resonances at $\delta = -4.7$ (small cage) and -8.3 ppm (large cage) are present, and the resonance of CH$_4$ molecules in a large cage is clearly seen below 3.0 mol% of tBuNH$_2$. Moreover, the number of encaged CH$_4$ molecules in the large cages of the double hydrate continues to increase as the concentration of tBuNH$_2$ decreases down to 1.0 mol%. In this region, when the aqueous tBuNH$_2$ solution was cooled below the phase boundary of pure CH$_4$ hydrate, it was found that pure CH$_4$ hydrate also formed as indicated by two resonances at $\delta = -4.3$ and -6.7 ppm, which are characteristic of CH$_4$ molecules trapped in small and large cages of sI hydrate, respectively. As the concentration of tBuNH$_2$ decreases, the amount of pure CH$_4$ hydrate formed becomes larger because the amount of water participating in the formation of the double hydrate decreases. In the case of 1.0 mol% of tBuNH$_2$, four NMR signals indicate the presence of CH$_4$ molecules enclathrated in each of the four hydrate cages of pure (sI) and double hydrate (sII). Therefore, Figure 3e precisely indicates the coexistence and guest distribution of CH$_4$ molecules in pure sI CH$_4$ hydrate and the sII double hydrate. In our experiments, the relative amount of sI and sII hydrate observed at low concentrations of tBuNH$_2$ is a variable that depends on the amount of excess water present and the reaction time. For practical purposes, it is desirable to work at a pressure that is just below the point at which sI hydrate appears. Therefore, the appearance of the spectra is not necessarily characteristic of the equilibrium distribution of the various hydrates. Note that the signal intensity in Figure 2 and Figure 3 does not directly represent the absolute amount of formed hydrates.

For several concentrations of tBuNH$_2$, the ratio of signal areas for CH$_4$ molecules in large cages to that of small cages of the double hydrates is plotted in Figure 4. As described above, the CH$_4$ molecules can occupy only the small cages of
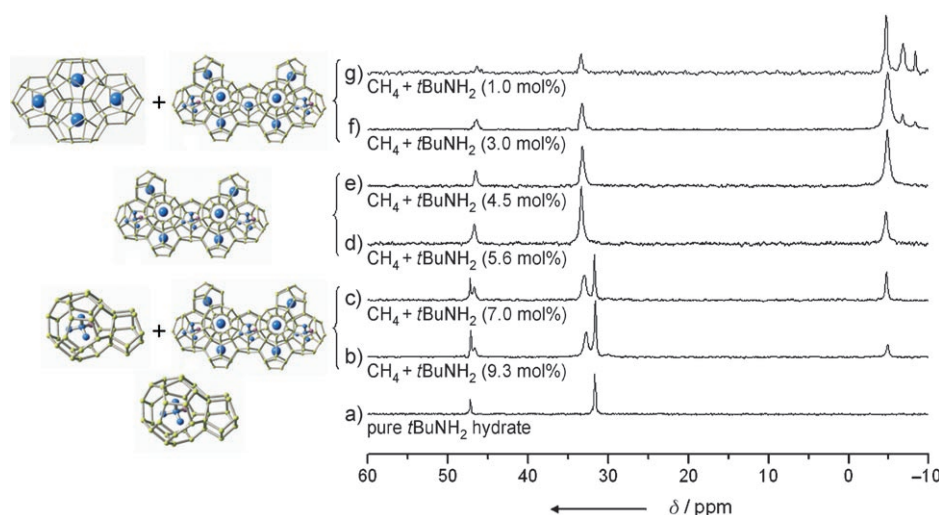
Figure 2. ¹³C MAS NMR spectra and structural diagrams of the pure and double hydrates: a) pure *t*BuNH₂ hydrate; b) and c) both pure *t*BuNH₂ hydrate and sII double hydrate coexisted (9.3 and 7.0 mol% *t*BuNH₂, respectively); d) and e) only the sII double hydrate formed (5.6 and 4.5 mol% *t*BuNH₂, respectively); f) and g) both pure sI CH₄ hydrate and sII double hydrate coexisted (3.0 and 1.0 mol% *t*BuNH₂, respectively). All samples, except for the pure *t*BuNH₂ hydrate, were prepared for NMR analysis by using the same experimental procedure (see text, Experimental Section, and Supporting Information for details). Hydrogen atoms were omitted in the structural diagrams.
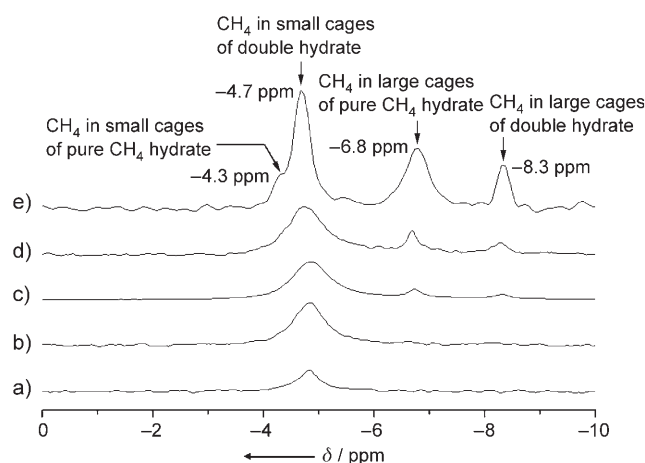
resulting values are shown in Figure 4. A value of 1.46, the lowest mole ratio of CH₄ to *t*BuNH₂ found, indicates that about 75% of the small cages are occupied by CH₄ molecules in the double hydrate; if all small and large cages encapsulate the CH₄ and *t*BuNH₂ molecules in the double hydrate, respectively, the mole ratio of CH₄ to *t*BuNH₂ becomes 2.0. As the concentration of *t*BuNH₂ decreases, the number of CH₄ molecules captured in cages increases. Based on the assumption that the occupancy of the small cage by CH₄ molecules is 0.75 (according to the result obtained for 5.6 mol% of *t*BuNH₂), the remaining CH₄ molecules should be confined in large cages of the double hydrate, which is about 31% of the large cages at 1.0 mol% of *t*BuNH₂.[18]
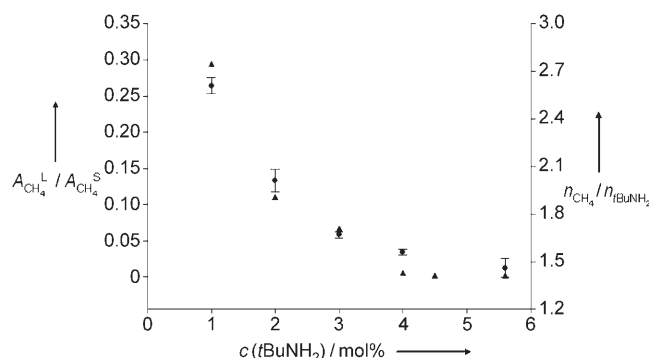

Figure 3. Expanded ¹³C MAS NMR spectra of double (CH₄ + *t*BuNH₂) hydrates. Concentrations of *t*BuNH₂: a) 5.6; b) 4.0; c) 3.0; d) 2.0; e) 1.0 mol%.

Figure 4. The area ratio (▲) of ¹³C MAS NMR signals for CH₄ molecules occluded in large and small cages and the CH₄/*t*BuNH₂ mole ratio (●) in the double hydrate.

the double hydrate up to 4.5 mol% but occupy both small and large cages of the double hydrate below concentrations of 4.0 mol% of *t*BuNH₂. The ratio of the integrated intensities for the two signals was 0.04 at 4.0 mol% but jumped to 0.294 at 1.0 mol% of *t*BuNH₂. To check the actual amount of CH₄ molecules stored in the hydrate phase, we measured the volume of CH₄ gas released from the double hydrate samples. The samples were prepared at 70 bar and 283.65 K to eliminate the possible formation of pure CH₄ hydrates that may result from a reaction between residual water and CH₄ gas in the low concentration region of *t*BuNH₂. The measured volume of CH₄ gas was converted into moles by considering the compressibility factor of the CH₄ molecule, and the

Thus, the amount of CH₄ in the sII double hydrate can be tuned by decreasing the concentration of *t*BuNH₂.

The results reported in this study show for the first time that a structural transition occurs in *t*BuNH₂ hydrate according to the initial concentration of *t*BuNH₂ when small molecules such as CH₄ are introduced. The structural transition was confirmed by PXRD and analysis of the solid-state NMR spectrum. At sufficiently low concentrations of *t*BuNH₂, pure CH₄ hydrate (sI) and double (CH₄ + *t*BuNH₂) hydrate (sII) coexist when crossing the corresponding phase boundary so that there is a complex mixture of solid phases. Moreover, it is shown that the storage capacity of CH₄ gas in the hydrate phase increases drastically as the initial concentration of *t*BuNH₂ decreases. These results confirm that the gaseous distribution of guest molecules and the hydrate composition can be altered by adjusting the concen-

Zuschriften

tration of the liquid guest. This "tuning mechanism" plays an important role in understanding the dynamics of hydrate cages and should be one of the strategies used to enhance the gas-storage capacity of double-hydrate systems, including a water-soluble liquid hydrate promoter for application to gas storage and transportation areas.

Experimental Section

The PXRD patterns were recorded at 113.15 K on a Rigaku Geigerflex diffractometer (D/Max-RB) by using graphite-mono-chromatized Cu$_{K\alpha1}$ radiation ($\lambda = 1.5406$ Å) in the $\theta/2\theta$ scan mode. The XRD experiments were carried out in step mode with a fixed time of 10 s and a step size of 0.05° for $2\theta = 10$–60°, thus rendering a total acquisition time of approximately 2 h for each hydrate sample.

To identify hydrate structure and guest distribution, a Bruker DSX 400 MHz solid-state NMR spectrometer was used. The powdered samples were placed in a zirconia rotor with an outer diameter of 4 mm, which was loaded into a variable temperature probe. The initial temperature (T) and pressure (P) were 293.15 K and 70 bar, respectively, and then T was gradually reduced to 270.15 K. The pure tBuNH$_2$ hydrate was made by freezing an aqueous solution of tBuNH$_2$ (9.3 mol%, the ideal stoichiometric concentration of tBuNH$_2$ hydrate) at 243.15 K. All ^{13}C NMR spectra were recorded at a Larmor frequency of 100.6 MHz with MAS at about 3 kHz. A pulse length of 2 μs and pulse repetition delay of 40 s under proton decoupling were employed with a radio frequency field strength of 50 kHz, which corresponded to 5-μs 90° pulses. The downfield carbon resonance signal of adamantane, which was assigned a chemical shift of $\delta = 38.3$ ppm at 300 K, was used as an external chemical shift reference. For the mixed hydrate samples, ^{13}CH$_4$ gas was used to obtain higher-intensity CH$_4$ signals.

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[18] In this case, by assuming that $\theta^S_{CH_4} = 0.75$ and $\theta^L = \theta^L_{CH_4} + \theta^L_{tBuNH_2} = 1$ due to stability of sII hydrate, we could determine the number of moles of guest molecules, CH$_4$ and tBuNH$_2$, in small and large cages of double hydrate, which was in agreement with $n_{CH_4}/n_{tBuNH_2} = 2.61$. From the resulting values, it appears that the final composition of double hydrate is $(12\,CH_4)_S \left(\frac{2.46\,CH_4}{5.54\,tBuNH_2}\right)_L \cdot 136\,H_2O$.